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US Army Research Laboratory

Resin Characterization

by Joshua Sadler, Ian M McAninch, Faye R Toulan, Felicia Levine, and John J La Scala

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14. ABSTRACT

The resin characterization standard process description outlines methods, specifications, and general information used to conduct resin characterization at the US Army Research Laboratory's Coatings, Corrosion, and Engineered Polymers Branch. Specifically, it defines methods for assessing whether resins meet desired Army properties using Dynamic Mechanical Analysis, Differential Scanning Calorimetry, Fourier Transform Infrared Spectroscopy, Nuclear Magnetic Resonance Spectroscopy, Scanning Electron Microscopy, Thermogravimetric Analysis, and Thermomechanical Analysis to analyze materials. This report defines a logical pathway by which we take a synthesized material through different testing phases in an effort to streamline the discovery of novel materials deemed acceptable for Army use. The basics of resins research are outlined for users in a concise manner that can be used to supplement a researcher's skill set.

15. SUBJECT TERMS

resin, characterization, competencies, standard process description, material properties

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Coatings, Corrosion, and Engineered Polymers Branch
Standard Process Description (SPD)

Resin Characterization

Resins/Polymers SPD #001
Origin Date: 07/28/2014   Rev. No. 0   Date: 06/22/2015

1.0   Purpose

This document provides guidance within the Resins/Polymers Process of the Coatings, Corrosion, and Engineered Polymers Branch, US Army Research Laboratory (ARL), on how to evaluate resins to ensure adequate understanding and knowledge of the resin system.

2.0   Scope

This standard process description (SPD) provides a general guideline for evaluating and understanding composite resins in the Coatings, Corrosion, and Engineered Polymers Branch. It is understood that this process is not applicable to every resin as some resins cannot be characterized by standard methodologies. Thus, some deviation from the process details is allowed given justification.

3.0   Policy

This SPD applies to all personnel developing and evaluating resins technology for composites applications in the Coatings, Corrosion, and Engineered Polymers Branch.

4.0   Responsibilities

The Coatings, Corrosion, and Engineered Polymers branch chief, Adhesives team leader, principal investigators, or the quality assurance coordinator will ensure that all personnel working on, developing, and evaluating resins have knowledge of this process before beginning relevant work within the branch.

5.0   Requirements

All researchers performing composite resins development and evaluation work in the Coatings, Corrosion, and Engineered Polymers Branch must use this SPD.

6.0   Acronym List

CTE: Coefficient of Thermal Expansion

DSC: Differential Scanning Calorimetry

DMA: Dynamic Mechanical Analysis

FTIR: Fourier Transform Infrared Spectroscopy

GPC: Gel Permeation Chromatography

T$_g$: Glass Transition Temperature

M$_c$: Molecular Weight between Crosslinks

NMR: Nuclear Magnetic Resonance Spectroscopy

PDI: Polydispersity Index

QSAR: Quantitative Structure-Activity Relationship

SEM: Scanning Electron Microscopy

E': Storage Modulus

TGA: Thermogravimetric Analysis

TMA: Thermomechanical Analysis

7.0   Records

Records will be kept in laboratory notebooks permanently and in computer records for 6 years.

8.0   Method

8.1   Overview

The method is a multitiered system whereby we down-select/screen resins according to each tier. The overall characterization process is depicted in the flow chart in Section 8.1.8.

8.1.1   The first tier involves resin sample preparation and determination of properties via survey dynamic mechanical analysis (DMA).

8.1.1.1   Resins are mixed and cured according to manufacturer or theoretical guidelines based on the documented molecular structure.

8.1.1.2   Molds are weighed immediately after filling with uncured resin. Molds are reweighed after resin cure to determine mass loss of volatile samples (e.g., vinyl esters, condensation polymers). Similarly, cured samples are weighed before and after postcure.

8.1.1.3   Survey DMA is performed by the method in Section 8.2.1 and IOP L1047-033. Only one sample thickness is used, nominally 3 mm, but it is at least consistent from sample to sample.

8.1.2   The second tier involves the following sets of procedures where molecular structure determination (8.1.2.1) is performed first and used to formulate the resin to prepare samples for the remaining tier-2 tests. There is no order of operation for the other tests in tier 2.

8.1.2.1   Molecular Structure Determination: Molecular structure determination can be obtained using information supplied by the vendor, collaborator, etc. If not supplied or additional information or confirmation is desired, molecular structure determination will be performed using gel permeation chromatography (GPC) according to IOP L1025-003 and IOP L1025-013, Fourier transform infrared (FTIR) spectroscopy according to IOP
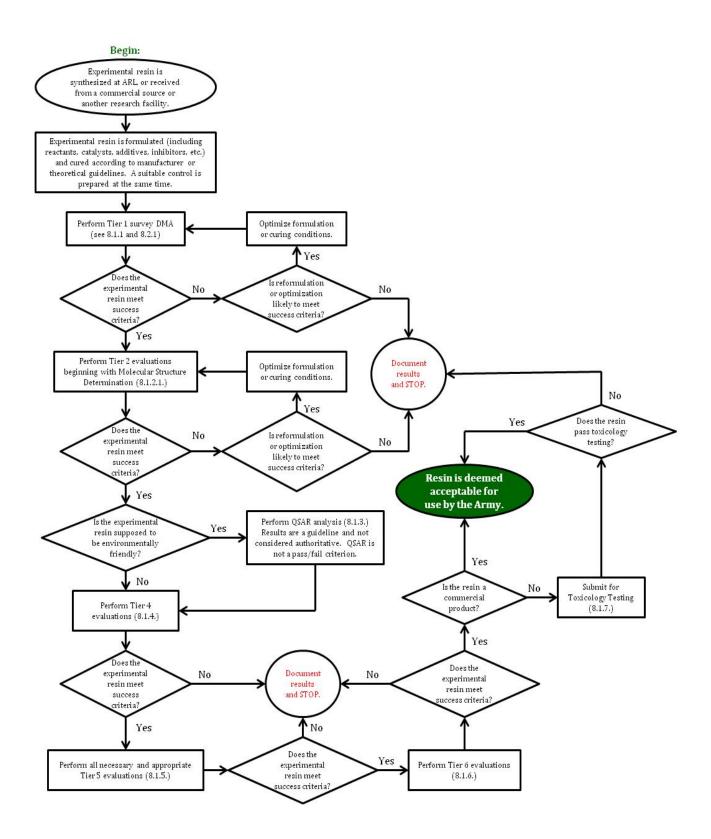
L1047-029 and IOP L1047-030, and nuclear magnetic resonance (NMR) spectroscopy according to IOP L1233-001 and IOP L1004-027 PicoSpin-45 NMR, or titration methods (if applicable) according to ASTM D 1652 (epoxy), ASTM D 2896 (base no.), and ASTM D664-11a (acid no.).

8.1.2.2 DMA**:** Determination of properties via DMA using IOP L1047-033 and information in Section 8.2.1.

8.1.2.3 Resin Viscosity: Resin viscosity is measured using AR2000 Rheometer IOP L1047-020.

8.1.2.4 Extent of Cure: Extent of cure is measured using FTIR according to IOP L1047-029 and IOP L1047-030 or differential scanning calorimetry (DSC) according to IOP L1047-034.

8.1.2.5 Thermogravimetric Analysis: Degradation temperature and sol content determinations are measured using thermogravimetric analysis (TGA) according to TGA 2950 IOP L1047-031 and TGA Q5000 IOP L1047-032.

8.1.2.6 Photographs of Samples: Photographs of the DMA samples, fracture toughness samples, and other samples, as desired, will be taken to show evidence of prepared polymers.

8.1.2.7 Surface Observations: Observations regarding the tackiness of the surface will be made after cure and after postcure. Tackiness shall be assessed using a gloved finger applying light pressure to the resin surface. The following rating scale shall be used to describe resin tackiness:

Rating	Description
0	Tack free. The surface has no apparent pull on the glove material.
1	Slightly tacky. There is some pull on the glove material.
2	Tacky. There is significant pull on the glove material.
3	Very tacky. Finger pressure leaves a permanent mar on the resin surface.
4	Extremely tacky. Resin transfers to the glove material.

8.1.3 For environmentally friendly resin technology development programs, the following additional procedure is required before commencing third-tier characterization experiments to ensure reduced toxicity relative to a baseline.

❖ Quantitative Structure-Activity Relationship (QSAR) analysis using the Environmental Protection Agency's Estimation Program Interface Suite model package to estimate physical properties, Toxicity Prediction by Komputer Assisted Technology (TOPKAT) to do human toxicity prediction, and possibly ECOTOX modeling system to estimate environmental toxicity or other modeling methods to predict properties/toxicity.

8.1.4 The fourth tier involves a more cumbersome measurement of materials properties and includes the following, in no particular order of operation:

8.1.4.1 Flexural Properties: Flexural strength and flexural modulus according to ASTM D 790.

8.1.4.2 Fracture Toughness: Fracture toughness according to ASTM D 5045. Optical photographs will be taken of all fracture surfaces at high-enough resolution to see plastic deformation of the surface.

8.1.4.3 Density: Density using the Archimedes principle (ASTM D 792).

8.1.4.4 Density as a Function of Temperature: Density change as a function of temperature and heat of expansion coefficient using thermomechanical analysis (TMA) according to ISO 11359-1 and ISO 11359-3, ASTM E831 and IOP L1047-016.

8.1.4.5 Optical Microscopy: Optical microscopy to examine morphology according to IOP L1118-006.

8.1.4.6 Scanning Electron Microscopy: Scanning Electron Microscopy (SEM) to examine morphology. There are written operating procedures for both of the microscopes in L1228, the Hitachi S-4700 finite-element SEM and the FEI NanoSEM 600. Users must be trained by a subject matter expert and sign the procedure documents once training has been completed. The SEM has many operational modes and parameters that can be tailored for a specific project and material requirements. After performing a standard alignment procedure, the user will systematically establish specific experimental parameters that best suit the material being evaluated.

8.1.4.7 Cure Kinetics: Cure kinetics is measured using FTIR according to IOP L1047-029 and IOP L1047-030 or DSC according to IOP L1047-034.

Additional measurements that can be performed at this tier of characterization include DMA multifrequency sweeps according to IOP L1047-033 and gel time determination (Sections 8.2.10 and 8.2.14 of this SPD).

8.1.5 The fifth tier involves more testing that is only required in some instances.

8.1.5.1 Water Absorption: Water absorption measurements are performed if water absorption is applicable to the material. Materials will be tested in a relevant environment, such that materials designed for naval or submerged use should be exposed to water at or near room temperature while materials for non-water use can be accelerated by performing water absorption experiments at elevated temperatures.

8.1.5.2 Chemical Exposure: Chemical exposure measurements are performed if applicable to the actual use of the material. Materials will be tested using only relevant, but safe, chemicals, such as JP-8, diesel fuel, other vehicle/aviation fluid, or common solvents. No heating is used in this method to accelerate the test.

8.1.5.3 Wet Glass Transition Temperature: Glass transition temperature (T_g) measurement after water saturation using DMA methodology according to IOP L1047-033 and analysis methods described below. DMA measurement of properties is required if water absorption is performed.

8.1.5.4 Wet Mechanical Properties: Flexural strength and fracture toughness after water saturation according to ASTM D 790 and ASTM D 5045. Mechanical testing of specimens is dependent on the application or customer requirements.

8.1.5.5 Ballistic Evaluation: Ballistic evaluation can be performed to evaluate the ability of the resin to withstand high-rate impact events.

8.1.6 The sixth tier involves measurements to enable a molecular understanding of the polymer network.

8.1.6.1 Continuous Soxhlet extraction or batch Soxhlet extraction of polymer sample to measure sol and gel fractions.

8.1.6.2 Reactivity Ratio Measurements for Multi-Reactive Site Vinyl Esters/Polyesters: To determine the "blockiness" of free-radically cured copolymer formulations using monomers with different reactive groups. This is irrelevant for epoxies and polyimides.

8.1.6.3 Morphology Characterization: To establish the morphology of the curing resin and identify whether highly crosslinked units are formed and interconnected or a more homogeneous network with no microgel morphology is determined.

8.1.7 The seventh tier involves testing of noncommercial resins/monomers for toxicology.

8.1.7.1 In vitro testing.

8.1.7.2 In vivo testing.

8.1.7.3 Aquatic toxicology.

8.1.7.4 Environmental toxicology.

8.1.8 The flow chart depicts the characterization process described in Sections 8.1.1–8.1.7.

Begin:

Experimental resin is synthesized at ARL, or received from a commercial source or another research facility.

↓

Experimental resin is formulated (including reactants, catalysts, additives, inhibitors, etc.) and cured according to manufacturer or theoretical guidelines. A suitable control is prepared at the same time.

↓

Perform Tier 1 survey DMA (see 8.1.1 and 8.2.1)

← Optimize formulation or curing conditions.

↓

Does the experimental resin meet success criteria? —No→ Is reformulation or optimization likely to meet success criteria? —Yes↑ (to Optimize formulation or curing conditions.)

—No→ Document results and STOP.

↓ Yes

Perform Tier 2 evaluations beginning with Molecular Structure Determination (8.1.2.1.)

← Optimize formulation or curing conditions.

↓

Does the experimental resin meet success criteria? —No→ Is reformulation or optimization likely to meet success criteria? —Yes↑ (to Optimize formulation or curing conditions.)

—No→ Document results and STOP.

↓ Yes

Is the experimental resin supposed to be environmentally friendly? —Yes→ Perform QSAR analysis (8.1.3.) Results are a guideline and not considered authoritative. QSAR is not a pass/fail criterion.

↓ No

Perform Tier 4 evaluations (8.1.4.) ← (from QSAR analysis)

↓

Does the experimental resin meet success criteria? —No→ Document results and STOP.

↓ Yes

Perform all necessary and appropriate Tier 5 evaluations (8.1.5.) → Does the experimental resin meet success criteria? —No↑ Document results and STOP.

—Yes→ Perform Tier 6 evaluations (8.1.6.)

↑

Does the experimental resin meet success criteria? —No→ Document results and STOP.

↓ Yes

Is the resin a commercial product? —No→ Submit for Toxicology Testing (8.1.7.)

↓ Yes

↑

Does the resin pass toxicology testing? —No→ Document results and STOP.

—Yes→ (up to) Is the resin a commercial product? —Yes↑

Resin is deemed acceptable for use by the Army.

6

8.2 Measurement of Properties

8.2.1 DMA

DMA is used to measure the T_g, rubbery modulus, and room temperature modulus of the polymer. Crosslink density, glassy modulus, damping, and breadth of glass transition may be characterized using this or other documented procedures, but the procedure must be defined along with the results. For all of the following measurements, at least 3 samples for each formulation should be tested; average and standard deviation shall be reported.

The following DMA testing parameters must be used: test frequency = 1 Hz, strain = 0.02%, heating rate of 2 °C/min with a temperature range that covers the glassy modulus (slow rate of decreasing modulus with temperature) through rubbery modulus (in the rubbery region, $T > T_g$, a rise in the modulus with increasing temperature should be measured unless sample degradation begins). If starting well below room temperature, the clamps should be retightened at the starting temperature. This prevents slippage of the sample in the grips resulting from thermal contraction.

Glassy Modulus: Glassy modulus is the storage modulus (E') at a defined temperature below the T_g. Room temperature modulus is E' at 25 or 30 °C. The temperature must be specified.

Maintain a sample length-to-thickness ratio of 10:1 or greater. Note that length refers to the testing span, not the sample's total length. Either dual or single cantilever will yield satisfactory results.

Typical sample dimensions:

35-mm dual cantilever clamp: $60 \times 12 \times 3$ mm
17.5-mm single cantilever clamp: $35 \times 12 \times 1.7$ mm

Glass Transition: T_g is measured primarily as the temperature at which the largest peak of the loss modulus occurs. Secondarily, T_g can be measured as the temperature at which the largest peak of the tan δ occurs or as the inflection point of the storage modulus in the glass transition region.

Rubbery Modulus: Single cantilever is the preferred clamp, as dual cantilever clamps can yield a continually decreasing rubbery modulus. The length-to-thickness ratio influences are not fully understood in the rubbery regime, but the sample *must* be thick enough to be within machine stiffness sensitivity limits.

Typical sample dimensions: 17.5-mm single cantilever clamp = $35 \times 12 \times$ up to 5 mm

Starting with a sample thickness of approximately 3 mm, perform DMA and evaluate the modulus values in the rubber region; note the general shape of the curve. Sample thickness may need to be adjusted to obtain optimal characterization of the rubbery region. Refer to the table below for guidance.

Rubbery Plateau Value of 3-mm-thick Sample	Recommended Sample Thickness to Try
50 MPa	2 mm
5 MPa	3.5 mm
2 MPa	5 mm

Rubbery plateau values: ~50 MPa: t ≈ 2 mm
~5 MPa: t ≈ 3.5 mm
~2 MPa: t ≈ 5 mm

The rubbery modulus is measured as the point at which E' in the rubbery region begins to increase with temperature. The molecular weight between crosslinks (M_c), inversely proportional to crosslink density, is estimated using Eq. 1:

$$M_c = 3RT\rho/E',\qquad\qquad(1)$$

where R is the ideal gas constant, T is the absolute temperature, and ρ is the sample density. If density values have not been measured, a sample density of 1 g/cm^3 is assumed and specified along with the calculated value.

Damping is measured by the area under the tan δ curve.

Breadth of glass transition is measured as the width of the loss modulus or tan δ peaks at half height.

When comparing different samples to each other, the user must follow the same exact procedures for a given measurement to be compared.

8.2.2 Measurement of T_g Using DSC

Samples are tested at heating rates of at least 10 °C/min to as much as 20 °C/min. The user must define the heating rate for all samples and remain consistent across the sample set. The higher heating rate is recommended for identification of T_g. The sample is heated to a prescribed temperature below the degradation temperature of the polymer (and below the melting temperature of aluminum [Al]), cooled to a temperature approximately 50 °C below T_g, and heated to another prescribed temperature below the degradation temperature of the polymer (and below the melting temperature of Al). The T_g is measured using Universal Analysis as the inflection point of the transition between the glassy baseline and rubbery baseline. At least 2 samples for each formulation should be tested; average and standard deviation shall be reported.

When comparing different samples to each other, the user must follow the same exact procedures for a given measurement to be compared.

8.2.3 Measurement of Extent of Cure Using DSC

Freshly prepare a small amount of resin (all desired components, initiators, inhibitors, etc.). Seal 5–10 mg of sample in a hermetic Al DSC pan and test according to the desired cure and postcure schedule. After the cure and postcure, quickly cool the sample to 0 °C or lower the temperature to quench the reaction, and then ramp the temperature at 5 °C/min to 300 °C to observe any residual cure, expressed as exothermic peaks. The total heat of cure is determined by taking 5–10 mg of freshly mixed uncured resin and ramping the temperature at 5 °C/min from room temperature to 300 °C. The area under the heat flow curve is the total heat of reaction. At least 2 samples for each formulation should be tested; average and standard deviation shall be reported.

8.2.4 Measurement of Extent of Cure Using Mid-FTIR

Samples should be prepared by grinding the uncured or cured material into a fine powder and then mixing at a concentration of 0.5–1.0 wt% with potassium bromide salt. Then, approximately 300 mg of the blended material is loaded into the salt press and pressed into a pellet using at least 7 metric tons of force for 2–3 min. At least 2 samples for each formulation should be tested; average and standard deviation shall be reported.

Resins, before cure and after postcure, are scanned in the mid-IR range of 1000 cm^{-1} to 4000 cm^{-1} at room temperature with a total of 64 scans per spectrum. Two peaks are to be measured: a peak representative of the reactive group and a reference peak that should remain relatively unchanged. If there is more than one component in the resin blend, then 2 peaks should be selected for each component and measured to assess the individual conversion of the constituents of the resin (each constituent may cure at a difference rate). Extent of cure can be calculated using Eq. 2:

$$\alpha = \frac{\left[\frac{ABS\ reactive}{ABS\ reference}\right]_{Uncured} - \left[\frac{ABS\ reactive}{ABS\ reference}\right]_{Cured}}{\left[\frac{ABS\ reactive}{ABS\ reference}\right]_{Uncured}} \ . \tag{2}$$

8.2.5 Measurement of Extent of Cure Using Near-IR

Untested DMA samples tend to be good samples for this method as their thickness of 3 mm is generally appropriate for near-IR measurement. The sample width and length must be larger than the IR beam, which can be as large as 1–2 cm. Samples are placed so that the IR beam passes in line through the 3-mm thickness dimension. Measurement and analysis are the same as for mid-IR. At least 2 samples for each formulation should be tested; average and standard deviation shall be reported.

8.2.6 Measurement of Molecular Structure Using FTIR

With libraries of known FTIR chemical spectra, we can use FTIR to identify the structural features of a molecule, such as epoxy, hydroxyl, vinyl, amine, and isocyanate. At least 2 samples for each formulation should be tested; average and standard deviation shall be reported.

8.2.7 Measurement of Molecular Structure Using NMR

With libraries of known NMR chemical spectra, we can use NMR to identify structural features of a molecule, such as epoxy, hydroxyl, vinyl, amine, phenyl, and alkyl.

Molecular weight of molecules can be measured through the analysis of repeat groups or end groups. Through a known internal or external standard peak, the ratios of peak integrals allow calculation of the relative numbers of various structural groups in the molecule. Given a known molecular structure, the number average molecular weight (M_n) of the molecule can be calculated easily.

8.2.8 Measurement of Molecular Weight Using GPC

GPC is used to evaluate the molecular weight and polydispersity index of the prepolymeric resins. Samples are processed using a Waters 717 plus Auto-sampler with a Waters 510 GPC using 3 columns set in succession, Phenogel 5μ 10^5 Å, Phenogel 5μ 10^3 Å, and Phenogel 5μ 500 Å. The columns are equilibrated at 40 °C before elution with helium purged tetrahydrofuran (THF) at a rate of 1.0 mL/min. The eluent is monitored using dual detectors: the first is a Waters 486 Tunable UV detector set to 230 nm and the second is a Waters 410 Refractive Index Detector both held at 40 °C. Samples are prepared by dissolving 1 mg/mL of polymer in THF, and molecular weights are calculated based on the retention time of polystyrene standards: 51,000 amu, 10,000 amu, 5,050 amu, and 580 amu.

8.2.9 Measurement of Degradation Temperature Using TGA

Samples of 10–20 mg are placed in a platinum pan and heated from 25 to 650 °C at a rate of 20 °C min^{-1} under an inert N_2 atmosphere (40 mL min^{-1} balance gas flow rate and 60 mL min^{-1} sample gas flow rate). The thermogram and the derivative thermogram should be plotted, and thermal stability factors, such as intial decomposition temperature (IDT), the temperature of 50% weight loss ($T_{50\%}$), and the temperature of maximum decomposition rate (T_{max}), determined by the maximum peak of the derivative thermogram.

At least 2 samples for each formulation should be tested; average and standard deviation shall be reported.

Sol content, the low molecular weight or soluble portion of the polymer network, can be estimated as the fraction of the mass lost below a certain prescribed temperature that is somewhat chemistry dependent but likely to occur at temperatures lower than 200–250 °C.

8.2.10 Measurement of Viscosity and Gel Time with a Rheometer

Sample prep. No initiator is added to resins for viscosity studies, but the initiator is added to resins for gel time studies.

The rheometer is used to measure viscosity using the steady-state flow experiment procedure listed in AR2000 Rheometer IOP L1047-020.

Gel time is measured on a rheometer using 1 of 2 methods: 1) steady-state flow experiment at a constant shear rate and 2) oscillatory experiments.

Both methods are performed holding the temperature constant using the environmental test chamber attachment to control temperature and disposable parallel plates. The experiment can be stopped when the sample viscosity increases to 100,000 cP or increases 2–3 orders of magnitude. It is strongly recommended that the user watch initial runs to ensure the rheometer is auto-stopping when its torque limit is reached and to prevent too high of an extent of cure that could make removal of the disposable plates from the rheometer problematic.

At least 2 samples for each formulation should be tested; average and standard deviation shall be reported.

8.2.11 Measurement of Properties Using TMA

Thermal expansion data in both the rubbery and glassy regions are measured using a thermomechanical analyzer. The coefficient of thermal expansion, CTE or α, is calculated by

$$\alpha = \frac{1}{l_0}\frac{\Delta l}{\Delta T}, \tag{3}$$

where l_0 is the original sample length, Δl is the change in length, and ΔT is the change in temperature. Samples should be made, following the cure procedure for the particular resin. Samples are generally small cylinders or rectangular cuboids; samples with nominal dimensions of $6 \times 6 \times 10$ mm have been found to be satisfactory, tested in the 10-mm direction, although other sizes can be acceptable. Regardless of sample size, care must be taken to keep the 2 sides in the measurement direction as parallel as possible; also, a larger dimension in the measurement direction increases the signal-to-noise ratio. A preload and applied load are necessary to maintain

probe contact with the sample; 0.05 N for both is satisfactory for epoxy-amine networks. Softer samples may require less force.

Heat the samples at 3 °C/min from room temperature to above the resin's T_g, then cool to –70 °C, or below the temperature of interest. Heat the sample at 3 °C/min again to the temperature of interest. The initial heating cycle is to remove any residual stress while the CTE value can be calculated from the expansion/contraction data from the final cycle using Eq. 3. Polymeric materials exhibit much larger CTE values above their T_g and this transition from a low to high CTE can also be reported as a measure of the T_g. T_g's measured by TMA may not precisely agree with those measured by DMA or DSC.

CTE values can also be used to calculate the density as a function of temperature (assuming isotropic behavior) and room temperature density, ρ_0, measured using the water displacement method outlined in ASTM D 792-00.

$$\rho(T) = \frac{\rho_0}{(1+\Delta)^3},\tag{4}$$

where $\Delta = CTE \times (T - T_0)$ in the same units of length as used in ρ_0.

At least 2 samples for each formulation should be tested; average and standard deviation shall be reported.

8.2.12 Cure Kinetics According to FTIR

FTIR is performed in accordance with IOP L1047-029 and IOP L1047-030. An FTIR operating in transmission mode with at least a 4-cm^{-1} resolution is used. A drop of the resin is sandwiched between two 25-mm-diameter sodium chloride disks (International Crystal Labs) separated by a 0.025-mm-thick Teflon spacer (International Crystal Labs) or pressed with potassium bromide (KBr) powder into pellets. The salt plate assembly, or KBr pellet, is placed in a cell holder. The temperature of the cell holder should be controlled to within ±0.1 °C of the set point. When the cell holder equilibrates to the desired cure temperature, the salt plate assembly is placed in the holder, and the first FTIR scan is taken. FTIR shall be run at set temperature until the cure is complete. Postcure should be performed by raising the set-point temperature to the desired temperature following cure. Postcure shall continue until the cure is complete. An FTIR spectrum comprising 16 scans shall be taken every 30 s during the cure reaction.

The conversion, α, is calculated by measuring the height of the peak relative to an internal standard (i.e., a group that is not affected by the reaction) (Eq. 5):

$$\alpha = 1 - \left(\frac{ABS(t)_{peak}}{ABS(t=0)_{peak}}\right)\left(\frac{ABS(t=0)_{s\tan dard}}{ABS(t)_{s\tan dard}}\right).\tag{5}$$

8.2.13 Cure Kinetics According to DSC

Samples are prepared as for FTIR cure kinetics experiments.

DSC can be used to determine the required cure duration for a given cure temperature. DSC has been used extensively for studying the cure kinetics of vinyl ester and polyester resins. The heat generated during the cure cycle, Q_T, and the heat generated during the final ramp, or the residual

heat, Q_R, are simply calculated as the area under the curve in the appropriate limits. The total amount of heat generated, Q_{tot}, is the sum of the heat generated during the cure and the residual heat. The extent of cure, α, is

$$\alpha = \frac{Q_T}{Q_{tot}}. \tag{6}$$

The rate of cure is

$$\frac{d\alpha}{dt} = \frac{1}{Q_{tot}}\frac{dQ_T}{dt}. \tag{7}$$

The rate of cure is useful for determining the rate constants of polymerization. The curing of vinyl esters and unsaturated polyesters with styrene is modeled as an autocatalytic process:

$$\frac{d\alpha}{dt} = \left(k_1 + k_2\alpha^m\right)\left(1-\alpha\right)^n, \tag{8}$$

where k_1 and k_2 are reaction rate constants and m and n are the reaction order. Equation 8 neglects k_1 and accounts for a final fractional conversion, α_u, being less than unity, and typically provides a more accurate fitting of the data.

$$\frac{d\alpha}{dt} = k\alpha^m\left(\alpha_u - \alpha\right)^n. \tag{9}$$

The total reaction order is assumed to be equal to 2. Therefore, only the rate constant and one of the reaction orders need to be determined experimentally. The rate parameters are calculated by fitting the model to the experimentally determined rate of cure as a function of conversion. The chemical similarity of the polymerizable groups between triglyceride-based resins and vinyl esters indicates that the curing of acrylated triglycerides should also be autocatalytic.

8.2.14 Gel Time Measurement

This test is designed to determine the working time of the resin before it solidifies into a gelatinous solid that no longer flows; at the gel point, the resin cannot further wet the fiber reinforcement in composites.

Samples are prepared by pouring 10 g of resin into a 30-mL screw-cap scintillation vial and adding appropriate amounts of initiator, catalyst, and inhibitor. Various samples are prepared using varying content of these initiator, catalyst, and inhibitor. In all cases, the inhibitor is added first. After mixing, the catalyst is added. Again after mixing, the initiator is added. Temperature is held constant throughout the experiment using an oven, hot plate, or similar equipment. The 10-g sample of resin will be maintained at this temperature until gelation. The sample is probed every 15 s with an applicator stick in the center of the material. When the resin no longer flows to fill in the void left by the applicator stick, the sample is considered gelled. The gel time is the elapsed time between mixing in the initiator and gelation. Two gel time samples will be run for each resin formulation, and times for both samples shall be reported.

8.2.15   Optical Microscopy

DMA samples can be fractured to expose the internal surfaces, or the fractured surfaces of the fracture toughness specimens can be used. Place the sample under the microscope objective and examine at low magnification, increasing to higher magnification. Use a standard imaging mode (not dark field) to determine the macroscale morphology of the sample. This method constitutes the use of regular optical microscopes and laser microscopes.

8.2.16   Scanning Electron Microscopy

DMA samples can be fractured to expose the internal surfaces, or the fractured surfaces of the fracture toughness specimens can be used. The surfaces should then be sputtered with a thin layer of gold using a sputter coater. A SEM should be used to image the surfaces at varying degrees of magnification from low to high to probe the microstructure.

8.2.17   Water Absorption

Water absorption experiments can be performed in 2 ways. The samples used should be premachined DMA samples or flexural and fracture specimens (no initiated crack, but notch should be present). No samples should be used with obvious defects, holes, visible porosity, etc., in excess of the average sample. The number of samples used depends on what is required for subsequent DMA and mechanical testing.

The first procedure is the water absorption at 30 °C. Samples are labeled individually. The samples are placed in a beaker or vat that is approximately two-thirds filled with water. All samples must be fully submerged. The vat/beaker is placed in a calibrated oven at 30 °C. Alternatively, the vat/beaker can be placed on a hot plate with the temperature being measured using a calibrated thermometer or thermocouple. Temperature variance of ±10 °C is acceptable during the experiment. Daily to weekly, depending on the absorption rate, the samples are removed from the beaker/vat, dried with a towel, and allowed to air dry for an additional hour to ensure all surface water is removed. The sample mass is measured and recorded. Ideally, samples would be measured daily, but because of weekends and slow water-absorbing samples, this amount of attention may be unnecessary. This experiment will continue for a minimum of 7 samplings and is completed once the last 3 measurements do not change by more than 0.1%. The average of the mass from the last 3 measurements is the final sample mass, m_f.

The second procedure is water absorption at 80 °C. The samples are placed in a beaker or vat that is approximately filled with water. All samples must be fully submerged. The vat/beaker is placed in a calibrated oven at 80 °C. Alternatively, the vat/beaker can be placed on a hot plate with the temperature being measured using a calibrated thermometer or thermocouple. A temperature variance of ±5 °C is acceptable during the experiment. Daily (except for weekends), the samples are removed from the beaker/vat, dried with a towel, and allowed to air dry for an additional hour to ensure all surface water is removed. The sample mass is measured and recorded. This experiment will continue for a minimum of 7 samplings and is completed once the last 3 measurements do not change by more than 0.1%. The average of the mass from the last 3 measurements is the final sample mass, m_f.

The elevated temperature procedure is the preferred method for materials that are not expected to be used in aquatic applications.

The water absorption percent for a sample is equal to m_f/m_0, where m_0 is the initial sample mass. The average and standard deviation shall be calculated and used for reporting purposes.

The rate of water absorption can be a useful property and is the derivative of the mass gain as a function of time during the initial linear stage of water absorption. The average and standard deviation shall be calculated and used for reporting purposes.

Qualitative hardness (to the touch), color changes, and opacity changes shall be noted.

8.2.18   Chemical Exposure

The samples used should be premachined DMA samples or flexural and fracture specimens (no initiated crack, but notch should be present). No samples with obvious defects, holes, visible porosity, etc., in excess of the average sample should be used. The number of samples used depends on what is required for subsequent DMA and mechanical testing.

The selected chemical depends on the chemicals and fluids the polymer is exposed to in operational use. Typical fluids include JP-8, diesel fuel, and transmission fluid. A recommended solvent to use is methyl ethyl ketone.

Samples are labeled individually. The samples are placed in a beaker or vat that is approximately two-thirds filled with the chemical. All samples must be fully submerged. The vat/beaker is tested at room temperature, which should be $23 \pm 5\,°C$ during the experiment. Daily to weekly, depending on the absorption rate, the samples are removed from the beaker/vat, dried with a towel, and allowed to air dry for an additional hour to ensure all surface chemical is removed. The sample mass is measured and recorded. Ideally, samples would be measured daily, but because of weekends and slow absorbing samples, this amount of attention may be unnecessary. This experiment will continue for a minimum of 7 samplings and is completed once the last 3 measurements do not change by more than 0.1%. The average of the mass from the last 3 measurements is the final sample mass, m_f.

The chemical absorption percent for a sample is equal to m_f/m_0, where m_0 is the initial sample mass. The average and standard deviation shall be calculated and used for reporting purposes.

The rate of chemical absorption can be a useful property and is the derivative of the mass gain as a function of time during the initial linear stage of water absorption. The average and standard deviation shall be calculated and used for reporting purposes.

Qualitative hardness (to the touch), color changes, and opacity changes shall be noted.

8.2.19   Ballistic Evaluation

Ballistic impacts are carried out with a 0.22-cal. gas gun at room temperature ($22 \pm 5\,°C$). A 5.56-mm-diameter steel ball bearing (Type 302, 0.69 g) shall be used as a projectile to impact the target. Projectile speed shall be tracked with a Doppler radar (BR-3502, Infinition Inc.) or another method. The polymer target (nominal $6 \times 6 \times 0.64$ cm) shall be sandwiched in a target frame with a circular opening of 5.08 cm in diameter. The projectile shall impact on the target surface with $0°$ obliquity. A witness plate (0.05-mm [0.002-inches]-thick 2024-T3 aluminum foil) shall be placed 2 inches behind the target. The witness plate shall be examined for penetration after each shot. Twelve targets shall be shot per specimen. The $V_{50}BL(P)$ ballistic performance shall be calculated by taking the arithmetic mean of the 3 highest nonpenetrating and the 3 lowest complete penetrating impact velocities on the witness plate.

8.2.20 Soxhlet Extraction

A cured resin sample is first broken into small pieces either manually or, preferably, using a cryogenic ball mill; smaller initial pieces reduce the total extraction time. A suitable sample size is often 5–10 g. Weigh the sample and a clean, dry cellulose thimble separately. Then weigh the thimble again after filling it with the resin. Place the thimble inside the Soxhlet extractor and reflux with an appropriate solvent. Acetone is a good solvent for most resin systems. Periodically (e.g., 24, 48, 72 h) stop the extraction, and remove, dry, and weigh the thimble to determine mass loss. Once the mass loss has stopped, stop the extraction. The mass loss divided by the initial mass is the soluble fraction. Alternatively, the solvent can be analyzed to determine the molecular weights, distributions, and species of the soluble portions.

8.2.21 Reactivity Ratio Measurements

Reactivity ratios are a measure of the likelihood of one component polymerizing with itself versus the other component (Eqs. 10 and 11):

$$r_1 = k_{11}/k_{12}. \tag{10}$$

$$r_2 = k_{22}/k_{21}. \tag{11}$$

r_1 is the reactivity ratio of component 1, k_{11} is the rate constant for the propagation of a radical of type 1 with a monomer of type 1, and k_{12} is the rate constant for propagation of a radical of type 1 with a monomer of type 2. When $r_1 = 0$, component 1 will only polymerize with monomer 2. When $r_1 = 1$, a radical of component 1 is equally likely to polymerize with either monomer. As $r_1 \rightarrow \infty$, radicals of component 1 will only polymerize with monomer 1.

The reactivity ratios are calculated using the Mayo-Lewis and the Fineman-Ross methods. Both methods use the copolymer equation in different forms to calculate the reactivity ratios. The copolymer equation for the Mayo-Lewis method is Eq. 12.

$$r_2 = \frac{x(r_1 x + 1)}{y} - x, \tag{12}$$

where x is the initial concentration ratio of component 1 to component 2 in the resin, and y is the initial concentration ratio of component 2 to component 1 in the copolymer. For particular values of x and y, values of $r_1 \geq 0$ are used to calculate r_2. The values of r_1 and r_2 are plotted, and the average intersection point of these lines for different x-y pairs gives the component reactivity ratios. The form of the copolymer equation for the Fineman-Ross method is Eq. 13.

$$x\left(1 - \frac{1}{y}\right) = \frac{x^2}{y} r_1 - r_2, \tag{13}$$

where a plot of x^2/y versus $x(1-1/y)$ has a slope equal to r_1 and an intercept equal to $-r_2$. The results should be similar for both methods and averaged to remove the effect of the calculation method.

8.2.22 Microgel Morphology

We do not have an established method to measure microgels currently. Researchers have shown that they could stop the cure of an unsaturated polyester or vinyl ester resins at low extents of cure and wash away the sol fraction using solvents to retain only the gel fraction. The gel fraction was

then analyzed using atomic force microscopy (AFM) that showed regions of high cross-link density (higher hardness) and regions of lower cross-link density (lower hardness). Alternatively, others showed that cured films could be degraded using a sodium hydroxide solution and then washed clean using water. The samples were then similarly analyzed using AFM. Experimental methods to assess microgel morphology may be developed and would be used to assess microgels.

8.2.23   Toxicity Testing

QSAR estimates are only a first step and are usually followed up by in vitro testing for parameters such as mutagenicity, neurotoxicity, and aquatic toxicity. These in vitro assessments have the inherent advantage of being relatively quick and much less expensive than in vivo animal testing. The predictive capability of in vitro testing is becoming increasingly important as countries worldwide attempt to reduce the use of live animals in toxicity testing. Individual compound tests typically take about 5 days each to run and are performed on bacterial cells (e.g., *S. typhimurium* or cell suspensions (i.e., "tissue culture") from mammalian systems (e.g., Chinese hamster ovary or liver cells) and can be performed for a couple of thousand dollars each. The endpoint varies with the individual test. In contrast, mammalian tests typically take from 14 to 90 days, depending upon the evaluation being performed, can consume dozens of animals, and cost several tens of thousands of dollars.

Once positive development decisions have been made, live animal in vivo testing is usually the last step. However, since these tests are very expensive, the fewer compounds that need be evaluated in this way, the more cost-effective the process. In vivo testing usually involves acute and chronic oral or inhalation toxicity testing, dermal and ocular sensitivity testing, mutagenicity, developmental or reproductive testing, and carcinogenicity testing performed in 2 species, usually rats and mice, although in some cases a nonrodent species is needed. Additional testing is often done for environmental degradation and wildlife toxicity testing (for protection of species covered by national laws or international treaties). Environmental testing is performed in a chemical laboratory setting, with the test compounds being exposed to environmental soil or water samples and chemically analyzed after a period of time. If wildlife testing is undertaken, birds are often the desired target, and bobwhite or Japanese quail are typically used.

ARL does not perform toxicity testing, so these experiments should be led by the Army Public Health Command.

9.0   References

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